Indian J. Phys. **64A** (4), 263-268 (1990)

Structural relaxation investigations by thermal expansion measurements in Se-Sb glasses

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Received 9 November 1989, accepted 18 April 1990

Abstract: Bulk samples of Se-Sb glasses were prepared by the melt quench technique. The familiar Wheatstone bridge involving metal foil strain gauges was used for the measurements of produced strain under the applied thermal stress. Investigations were made for the glass structural relaxation and the results revealed both the glass and crystallization (hexagonal Se and trigonal Se_3Sb_2) transitions. It has also been observed that the Sb-content affects both the strain level and the locations of the above transitions, i.e. the more content of Sb leads to increase the strain level and shifting the position of the glass transition as well as that of Se_3Sb_2 crystals to a higher temperature. Besides, the effect of annealing on the thermal expansion has also been investigated.

Keywords: Se-Sb glass, structural relaxation, glass and crystallization transitions.

PACS Nos: 64.70.D, 64.70.pf, 65.70.+y

1. Introduction

Atomic vibrations, in amorphous materials, are affected by the atomic arrrangement and the bond strength in the matrix. Therefore, the thermal properties, such as, thermal expansion coefficient are of great interest for understanding the amorphous structure.

It is known that (Komatsu *et al* 1985) metallic glasses prepared by various rapid quenching techniques, are thermodynamically unstable and tend to relax toward more stable structures during annealing well below the glass transition temperature (T_g) and finally lead to crystallization. This structural relaxation affects various physical properties, such as, magnetic, electrical and thermal properties.

Several studies on the thermal expansion behaviour of metallic glasses have been reported (Chen *et al* 1973, Brooks 1978, Shelby 1979, Steinberg *et al* 1980 and Komatsu *et al* 1983). All results showed that the thermal expansion behaviour of some metallic amorphous alloys is similar to that of oxide glasses. Also, the structural relaxation representing both of the topological and the compositional

short-range ordering (Egami 1978a,b, Graham and Egami 1978) leads to several changes in properties, such as, densification, the increase in the Young's modulus (Chen 1978) and Curie temperature (Liebermann *et al* 1977).

Egami *et al* (1981) and Strolovitz *et al* (1981) proposed the defect model by the atomic level stresses as the microscopic model of structural relaxation in metallic glasses. They found that a small change of about 0.5% in the density occurs as a results of the anharmonicity of the interatomic potentials. However, experimental data on the thermal expansion coefficient of metallic glasses are not fully available on the contrary to other data, such as, magnetic, electrical and mechanical properties. Therefore, it is very interesting to study here structural relaxation of the Se-Sb glasses through the measurements of thermal expansion under the applied thermal stress.

2. Experimental techniques

Amorphous bulk samples of the system $Se_{100-x}Sb_x$, where $x=7.5$, 12.5 and 22.5 were prepared by the usual melt-quench method. The high purity constituents (99.99) were mixed together, in desired proportions in silica ampoules which are then sealed off at 10^{-4} cm Hg. The sealed ampoules were inserted in an electric furnace held at 850°C and maintained inside it for two hours. During heating, the tubes were frequently shaken to ensure homogeneity of the melt. Then the tubes were quenched in an ice-water and specimens of cylinderical shape (one cm long and 0.8 cm diameter) were prepared. The amorphous state of tested samples was confirmed by X-ray diffraction.

Metal foil resistance gauges (type HG 732 C 6EL) were cemented onto the tested specimens and the familiar Wheatstone quarter bridge arrangement (Vaughan 1975) was used to measure strain. Two resistors, each of 350Ω were connected in two arms of the bridge and two similar strain gauges (each of $350 \pm 1\Omega$ and gauge factor $K=2.16 \pm 1\%$) were connected into the other two arms. One of the gauges was cemented on the surface of the specimen with its length parallel to the specimen axis and used as an active gauge, to measure the strain, on the surface of the specimen due to the applied thermal stress. The second gauge was a dummy used for temperature compensation and suspended freely in the furnace. For the bridge, the out-of-balance voltage V is related to the strain ϵ as follows (Vaughan 1975):

$$\epsilon = \frac{4V}{EK}$$

where, E, is the applied voltage to the bridge.

In all measurements, the temperature of each tested specimen was raised at a nearly constant rate (1 K/min.). The readings were recorded for every 5 degrees in

temperature and the corresponding values of strain were calculated. The results obtained for strain variation with temperature were corrected for the gauge factor and bond material.

3. Results and discussion

(i) Strain dependence on temperature in the Se-Sb glasses :

Figure 1 shows the variation of strain, ϵ, with temperature for the system $Se_{100-x}Sb_x$ where $x = 7.5$, 12.5 and 22.5. This figure shows that the curves of all investi-

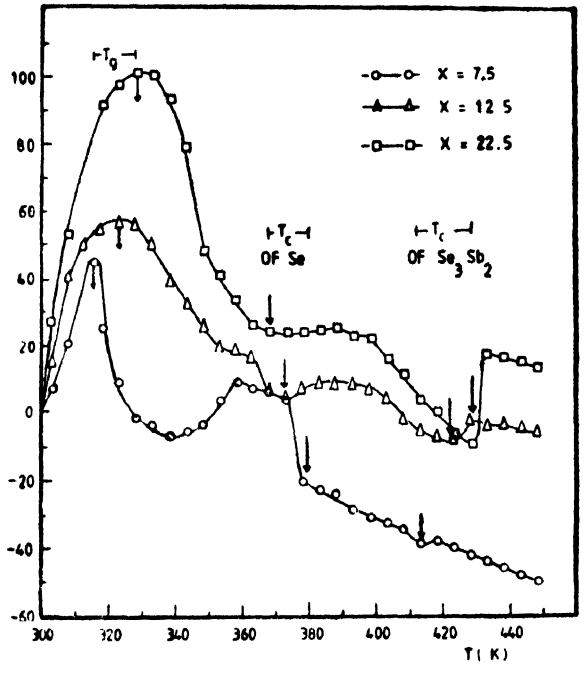

Figure 1. The variation of strain, ϵ, with temperature for the system $Se_{100-x}Sb_x$ where, $x = 7.5$, 12.5 and 22.5.

gated samples have same generality but with different levels of observed strain. For each tested specimen, the strain showed to be increased, at first with the increase in temperature. This may be due to the ability of tested glasses to be relaxed toward more stable structure below their glass transition temperatures (Steinberg *et al* 1980 and Komatsu *et al* 1985) as caused by the irreversible changes in the excess volume of the non-ideal amorphous alloys. Beyond the glass-transition region, the strain has decreased with increasing temperature and all curves showed maximum points indicating the positions of glass-transition temperatures specified for the specimens under work (Figure 1).

A significant parameter that determines the rate of crystallization of some chalcogenide glasses (Chaudhari and Herd 1972) is the change in density on

crystallization and the volume of the crystalline phase is usually less than that of the glassy one. Thus in the temperature range above the glass transition region, the strain has decreased with temperature and two troughs occurred in each curve, represent the crystallization temperature of each sample (Figure 1). In the crystallization region, the strain decreased and reached a negative value indicating a shrinkage in the volume of worked glasses after being crystallized. However, the positions of transition temperatures which obtained here by our strain measurement are compared with those reported previously (El-Zaidia et *al* 1987) by DTA on some $Se_{100-x}Sb_x$ glasses as shown in Table 1. The observed shifts in temperatures of

Table 1. Glass and crystallization temperature of $Se_{100-x}Sb_x$ glasses.

	Rate (K/min)	T_g(K)	T_c(K)	Technique of measurement
5	10	334.5	410	
10	10	320.5	409	DTA
15	10	324	405	
7.5	1	316	378, 412	
12.5	1	325	370, 422	Strain measurement
22.5	1	330	368, 428	

both T_g and T_c may be attributed to the fact that not same compositions and heating rates were used in two work.

(ii) Strain dependence on composition in the Se-Sb systems :

The Se-Sb systems can be pictured (Giridhar et *al* 1980) to be made up to cross-linked three dimensional structural units of trigonal Se_3Sb_2 phase distributed among other constituent phases of the polymeric selenium chains and the minor Sb phase. Thus, the compositional dependence of the investigated Se-Sb glasses on the Sb content can also, be seen from Figure 1. It was observed that the addition of Sb atoms in the specimen does affect, not only the strain level, but also the position of both the glass and crystallization transition temperatures.

In the glass transition region the modulus of the glassy state decreases to a great extent, as indicated by the increase in the strain with the incrcease in temperature. As shown in Figure 1, this increase in the strain becomes considerable as the Sb content increases, because the latter may facilitate the softening of the glass of the non-crystalline regions of Se under the structural restraint of molecular chains in the cross-linked trigonal Se_3Sb_2 regions with the increase in temperature. As a result of these structural restraints, there is a tendency for the position of the strain peak to shift to higher temperatures (from 316–330 K) when they are increased with the increase of the Sb content. This has been observed previously (Abo-Ghazala et *al*, to be published) by the internal friction investigations for same glasses and confirmed here by the strain measurements.

For specimens after being relaxed in the glass transition region, the molar volumes have been decreased showing decrease in the measured strain and two troughs obtained in the ranges 368 to 378 and 412 to 428 K in each curve of Figure 1. These may be attributed to different crystal structures (El-Zaidia *et al* 1987), the hexagonal Se crystallites and the trigonal Se_3Sb_2, respectively. It is obvious to note that the occurrence of these troughs is in converse sense to each other, i.e., addition of Sb atoms to the specimens shifts the trough representing the Se hexagonal structure to lower temperatures and decreasing its depth. While, the increase in the Sb content was leading to the growth of Se_3Sb_2 trigonal regions. Thus, a trough of large magnitude is obtained with its location being shifted to higher temperatures due to the structural restraints associated with these trigonal units.

Besides the above transitions, which were observed for all tested glasses, only the specimen $x=7.5$ shows another trough in the strain curve at a temperature 340 K. The appearence of this trough for this specimen of less Sb content is probably due to an unhomogeneity of this glass and the differences in bond-strengths, since the weakness of Sb-Sb and Se-Sb compared to Se-Se bond-strengths was observed (Giridhar *et al* 1980). Anyhow, a similar behaviour was observed (El-Zaidia *et al* 1987) by DTA thermograms on Se_{100-x} Sb_x glasses. Those results revealed sharp endothermic and exothermic peaks for both the glass and crystallization transitions of specimens with $x=10$ and $x=15$ respectively. While, the case in which $x=5$, a rather spread endothermic peak corresponding to its glass transition appeared.

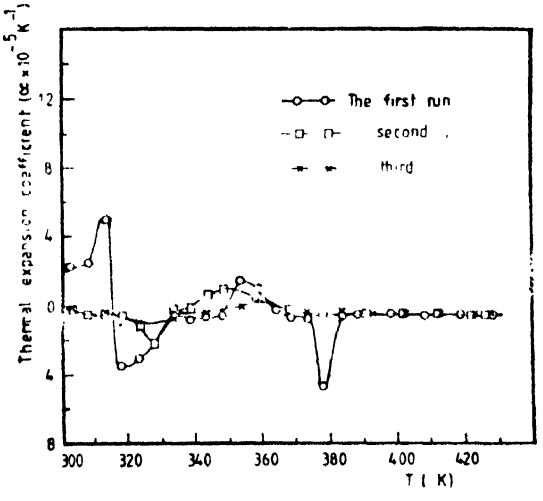

Figure 2. Effect of annealing on thermal coefficient of linear expansion of the system $Se_{92.5}Sb_{7.5}$.

The effect of thermal cycling during heating on thermal expansion behaviour was investigated for the specimen with $x=7.5$. The results obtained are shown

in Figure 2. In the first-run plot the thermal expansion coefficient increases up to 316 K. Then it is abruptly decreased to a negative value in the temperature region during which the glass transition has occurred. After that it is increased again with temperature up to 375 K where another sudden decrease corresponding to crystallization temperature of hexagonal Se regions is observed. Beyond this limit till the end of measurement, the expansion coefficient seems to be constant with temperature and no trough corresponding to Se_3Sb_2 trigonal regions is obtained. This is perhaps due to the presence of few amount of these units in the studied sample which has no great effect on the specimen volume. The plots representing the second and third runs are nearly similar. They show a small decrease in the thermal expansion coefficient with temperature in the glass transition region and then an increase to coincide with that of the first-run plot with no appearance for any crystallization transition. This may be attributed to the transformation of the whole specimen into the crystallized phase.

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